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THEORY OF THE LIQUID STATE AND THE PHYSICAL INTERPRETATION OF HUDLESTON'S EQUATION

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ABSTRACT

It is argued that the statistical and quantum mechanics of the solid represent a proper point of departure in determining the properties of the liquid state near the fusion curve, or at high pressure but sufficiently low temperature, in conformity with the views of Frenkel. On this basis, Hudleston's equation of state is interpreted physically as corresponding to a model of independent bond oscillators, with the effect of anharmonicity for either the solid or liquid taken into account by means of the Grüneisen theory of lattice vibrations. The model yields a derivation applying to the solid in any event, and valid approximately for a liquid either near the crystallization point, or at high pressure and low temperature. In this manner, the two parameters α and β entering the corresponding law of intermolecular force are evaluated in terms of a characteristic frequency and the Grüneisen constant, respectively. The generalization of Hudleston's equation to include the effect of variable temperature is given; it includes a correction factor essential to a correct result, but not appearing previously in the literature. The Hudleston parameter B in the equation of state as derived theoretically is expressed in terms of the Grüneisen constant, explaining the insensitivity of this parameter to temperature, as observed experimentally. On

the basis of the Debye theory for solids and an extension to liquids, a variant form of Hudleston's equation is derived, which takes into account coupling of the vibrations of the atoms or molecules. This result is generalized to arbitrary temperature also. The Grüneisen constant determined from the experimental value of B for liquid mercury is compared with values inferred from Grüneisen's law and from compressibility parameters, and reasonable agreement is found. Finally, an explicit demonstration is given of the close correspondence between Hudleston's equation of state for a liquid and Bardeen's quantum mechanical result for a solid, in the case of the alkali metals near fusion.

INTRODUCTION

An equation of state given by Hudleston¹ has been used with

(1) L. J. Hudleston, Trans. Faraday Soc., **33**, 97 (1933).

considerable success in correlating the experimental data for the pressure vs. the volume in many liquids.²⁻⁴ With respect to the intermolec-

(2) K. E. Bett, J. Imperial College Chem. Eng. Soc., **7**, 44 (1953).

(3) K. E. Bett, P. F. Hayes, and D. M. Newitt, Phil. Trans. Roy. Soc., **A247**, 59 (1954):

(4) K. E. Bett, K. E. Weale, and D. M. Newitt, British J. Appl. Phys., **5**, 243 (1954).

ular force law selected, Hudleston's discussion gives no physical basis for the particular analytic form chosen, but only for the argument of the function. The purpose of this paper is to explain the success of the

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corresponding equation of state by obtaining it from a definite physical model. A variant form is derived which has certain theoretical advantages.

The basis of the theoretical discussion is the Grüneisen theory of lattice vibrations.^{5,6} The success of this theory in explaining the

(5) E. Grüneisen, "Handbuch der Physik," Vol. X, Verlag Julius Springer, Berlin, 1926, pp. 1-59.

(6) J. C. Slater, "Introduction to Chemical Physics," McGraw-Hill Book Co., Inc., New York, N. Y., 1939, pp. 201, 222, 238, 394, 451.

thermal expansion of solids as the result of anharmonicity of the characteristic oscillations is well known. However, Hudleston's equation has been tested experimentally only for liquids. Since application of the Grüneisen theory to a liquid involves an extension of its domain of validity as usually understood, a prefatory discussion of the grounds for this extension will be given.

THEORETICAL BASIS

In Mayer's theory of cluster integrals, the distribution for which a very large fraction of all the molecules are in one cluster corresponds to the liquid state.⁷ The cluster integral for this distribution is far

(7) J. E. Mayer and M. G. Mayer, "Statistical Mechanics," John Wiley and Sons, Inc., New York, N. Y., 1940, Chapters 11, 13, 14.

too complicated to be evaluated directly (and in any event the corresponding series diverges at the liquefaction point). Severe calculational

difficulties appear in the theories of Born and Green⁸ and of Kirkwood⁹

(8) M. Born and H. S. Green, "A General Kinetic Theory of Liquids," Cambridge University Press, Cambridge, 1949.

(9) R. W. Swanzig, J. G. Kirkwood, K. F. Stripp, and I. Oppenheim, J. Chem. Phys., 21, 1268 (1953).

near the crystallization point. As a consequence, resort commonly is made to free-volume or to lattice theories (of the cell or hole type) for a liquid.¹⁰ These methods entail underlying approximations restricting

(10) J. O. Hirschfelder, C. F. Curtiss, and R. B. Byrd, "Molecular Theory of Gases and Liquids," John Wiley and Sons, Inc., New York, N. Y., 1954, Chapter 4.

their range of validity, the precise nature of which has been elucidated by Kirkwood.¹¹

(11) J. G. Kirkwood, J. Chem. Phys., 18, 380 (1950).

In these circumstances, one can suggest that a proper point of departure in determining the properties of the liquid state near the fusion curve is the statistical mechanics of the solid. This viewpoint has been stressed particularly by Frenkel.¹² He points out that fusion

(12) J. Frenkel, "Kinetic Theory of Liquids," Oxford University Press, Oxford, 1946, Chapter III.

is accompanied by only a relatively small increase of volume, showing that the arrangement of the molecules in a liquid near its solidification point must be similar to the arrangement in the corresponding solid, as regards nearest neighbors. Further, the specific heat capacity of a

liquid is only slightly greater than that of the solid, in general. Finally, the latent heat of fusion is much smaller than the latent heat of vaporization. More important is a fact not noted by Frenkel, that the latent heat of fusion is small relative to the cohesive energy of the solid. These facts imply that the cohesive forces between the molecules decrease only slightly at fusion, corresponding to the very slight amount by which the average distance apart of the molecules is increased. It follows that near the solidification point, the free energy of the liquid must be similar in analytic form to that of the solid, as well as numerically equal in the case of the Gibbs free energy. The conclusion follows that the equation of state of a liquid near the melting point must be closely similar to that of the corresponding solid. This important conclusion will be demonstrated directly from equations of state in the penultimate section.

The general contentions of Frenkel are supported by the evidence from structure analyses by X-rays of liquids and solids near the fusion temperature. These data have been summarized conveniently by Darken and Gurry.¹³ The over-all results of these experiments point to a loss in

(13) L. S. Darken and R. W. Gurry, "Physical Chemistry of Metals," McGraw-Hill Book Co., Inc., New York, N. Y., 1953, Chapter 5.

the liquid near the solidification point of the long-range order characteristic of the solid but with preservation of a considerable degree of short-range order. It is the similarity in the short-range order in the two phases which leads to the close correspondence between many thermodynamic quantities. Only a quantity, such as the rigidity, which depends

intrinsically on order of long range will be grossly different for the two phases (even in this case gradations are possible, corresponding to the existence of the visco-elastic solid). In general, one expects the similarity of the liquid and solid to hold approximately so long as the coordination number has a well-defined meaning.

From the standpoint of quantum mechanics, one can consider the total wave function decomposable in some sense into contributions from individual atoms. For a particular atom, the presence of long-range order in the solid will result in only small overlap of its wave function with those for distant atoms. Thus, a quantity like the internal energy will be sensitive mainly to the near-neighbor atoms involved in the short-range order, where the overlap of the wave functions is significant. Because of the small change in linear dimensions at fusion, the degree of overlap of wave functions must be very similar for the two phases. This argument applies in the first instance at the fusion point, but clearly implies that a liquid at high pressure but sufficiently low temperature with state coordinates considerably removed from the fusion curve also behaves thermodynamically in a manner similar to a solid.

It is worthy of note that the correspondence between thermodynamic functions for the two phases near the melting point can be extended to transport properties also. The change in electrical conductivity at fusion has been discussed theoretically by Mott¹⁴ and the viscosity of

(14) N. F. Mott, Proc. Roy. Soc., A146, 465 (1934).

liquids near the melting point has been treated by Andrade,¹⁵ taking

(15) E. N. da C. Andrade, Proc. Roy. Soc., A211, 12 (1952).

properties of the solid as a point of departure. Both authors assume that the atoms (or molecules) of a liquid vibrate about mean positions which are not fixed, as in a solid, but move with a velocity small compared to the velocity of vibration. As a legitimate first approximation, therefore, both authors assume that the drift velocity of the equilibrium positions vanishes, which is tantamount to viewing the liquid as a solid in the sense of the Grüneisen theory, with respect to thermal excitation. Mott evaluates the characteristic frequency of the liquid by regarding it as an amorphous solid on the Debye theory, and obtains a result for the change in electrical conductivity at fusion which is in good agreement with experiment, in general. On the other hand, Andrade identifies the characteristic frequency of the liquid as the Lindemann frequency appropriate to the solid at melting, to yield a result which represents reasonably the viscosity of a liquid near the melting point.

The following derivation of Hudleston's equation applies to a solid in the first instance. The extension to a liquid rests broadly on the general principles enunciated by Frenkel and the discussion above, and specifically on the models of Mott and Andrade. Thus, the atoms are assumed to vibrate as in a solid, with the centers of vibration fixed, as a first approximation. The derivation proceeds by evaluating the energy required to compress the body against the restoring force of these oscillators at zero temperature. Since this method does not yield an explicit expression for the free energy, the effect of variable temperature in Hudleston's equation is determined by means of a phenomenological

theory given by Gilvarry.^{16,17} In what follows, it will be assumed when

(16) J. J. Gilvarry, J. Appl. Phys., 28, 1253 (1957).

(17) J. J. Gilvarry, J. Appl. Phys., 33, 3595 (1962).

necessary that the frequency spectrum of a liquid is of Debye form in the sense of Mott's approximation. The treatment given goes beyond the approximations of Mott and Andrade, in the sense that anharmonicity of the characteristic vibrations of the liquid is taken into account on the basis of the Grüneisen theory.

Note that the cell method has points in common with the Debye theory or the corresponding Einstein form applied to a liquid, as discussed by Mayer and Mayer.⁷

HUDLESTON'S EQUATION

Hudleston postulates a repulsive force f between two molecules as

$$f = \alpha(r_0 - r)e^{\beta(r_0 - r)} \quad (1)$$

where r_0 is the value at zero pressure of the intermolecular distance r , and α and β are positive constants specific to the material. For a cubical specimen of edge length L , the pressure P is proportional to f/L^2 . In the literature, the corresponding equation of state generally appears as

$$\log_{10}[L^2P/(L_0 - L)] = A + B(L_0 - L) \quad (2)$$

where L_0 is the value of L for zero pressure, and A and B are positive constants. The parameter A can be evaluated as

$$A = \log_{10}(3L_0K_0) \quad (3)$$

in terms of the bulk modulus K_0 for zero pressure. Note that the values of the Hudleston parameters A and B in eq. 2 depend on the units used for P and L . However, the former variables enter a linear form equated to a logarithmic function whose argument is not dimensionless, and hence definite dimensions cannot be assigned to A and B on the basis of eq. 2. It is common in the literature to evaluate the length L in terms of the cube root of the ratio to a reference value of the volume at a particular pressure and temperature, by a procedure which amounts to regarding L (and L_0) as dimensionless, in which case A and B can be viewed as dimensionless also. In spite of these difficulties, eq. 2 has the merit that the parameters A and B can be determined readily if a plot of the data corresponding to the two sides of the relation yields a straight line.

The discussion given by Hudleston was frankly semi-empirical. Thus, he failed to state whether or not he regarded r and r_0 in eq. 1 as thermal averages. Further, he made no mention of an attractive force between the molecules, nor of the fact that f of eq. 1 reverses sign when r exceeds r_0 .

CASE OF ZERO TEMPERATURE

To understand Hudleston's results, consider the molecules of the liquid or atoms of the solid at zero temperature as interacting in pairs, and assume that each such pair is independent. The two molecules in each bond will have a characteristic frequency ν whose variation with

respect to volume V can be specified by introducing the Grüneisen parameter γ , defined by^{5,6}

$$\gamma = -\partial \ln \nu / \partial \ln V \quad (4)$$

specifically for a solid and by extension for a liquid. To first order, the variation with respect to volume of the frequency of an oscillator is then given by the definition 4 as

$$\nu = \nu_0[1 + \gamma_0(V_0 - V)/V_0] \quad (5)$$

where ν_0 and γ_0 are the frequency and Grüneisen parameter, respectively, evaluated at the volume V_0 corresponding to zero temperature and pressure. Using reduced coordinates, one can then express the potential energy u of a bond oscillator of variable frequency (and force constant) as the truncated Taylor series¹⁸

(18) J. J. Gilvarry, Phys. Rev., 102, 331 (1956).

$$u = \pi^2 m \nu_0^2 (r_0 - r)^2 [1 + 2\gamma_0(r_0 - r)/r_0] \quad (6)$$

in terms of the intermolecular distance r , if m is the mass of a molecule.

At sufficiently low temperature, the mean thermal energy (potential and kinetic) of an oscillator becomes small relative to u of eq. 6, provided that the zero-point energy can be ignored in comparison with u . The last condition is met for only very slight compressions, since ν_0 enters the zero-point energy linearly but appears in eq. 6 quadratically. Hence, eq. 6 represents the total energy associated with a bond in this case. Since the discussion at this point is restricted to the case of

zero temperature, r and r_0 in eq. 6 do not necessarily represent averages over thermal fluctuations, or ensemble or time averages (at least in the sense of classical statistics). They may be regarded as coordinates of an individual oscillator.

The total potential energy u of eq. 6 yields the force

$$f = 2\pi^2 m v_0^2 (r_0 - r) [1 + 3\gamma_0 (r_0 - r)/r_0] \quad (7)$$

on differentiation. From Hudleston's expression 1, one obtains

$$f = \alpha (r_0 - r) [1 + \beta (r_0 - r)] \quad (8)$$

for $r_0 - r$ small, by expansion of the exponential and retention of terms through linear. Comparison of the two results yields

$$\alpha = 2\pi^2 m v_0^2 \quad (9)$$

$$\beta = 3\gamma_0/r_0 \quad (10)$$

which provide a physical interpretation of the Hudleston parameters α and β in terms of the frequency ν_0 and Grüneisen parameter γ_0 , respectively. Thus, Hudleston's model corresponds to representing the liquid or solid as an assemblage of independent anharmonic oscillators. Note that the spring forming a bond is nonlinear, since the force constant increases with compression, in agreement with the sense of the variation predicted by the Grüneisen theory.

The change in energy E at zero temperature of the compressed solid or liquid from its value for zero pressure can be expressed as

$$E = 3Nu \quad (11)$$

if N is the number of atoms or molecules. The coefficient of u is necessarily $3N$, since each oscillator introduces a generalized coordinate $q = r_0 - r$ to describe a bond, and $3N$ is the number of degrees of freedom (in the absence of molecular rotation). The volumes can be written in terms of the corresponding molecular separations as

$$V = cNr^3 \quad (12)$$

$$V_0 = cNr_0^3 \quad (13)$$

where c is a constant. For solids, c is unity for a simple cubic lattice, and values for other lattice types have been given by Slater.⁶ In the case of a liquid, c obviously depends on the average coordination number.

Differentiating eq. 11 with respect to volume, one obtains

$$P = 3K_0[(V_0/V)^{2/3} - (V_0/V)^{1/3}] \quad (14)$$

as the dominant contribution to the pressure, to be multiplied by the correction factor

$$1 + 3\gamma_0[1 - (V/V_0)^{1/3}] \quad (15)$$

corresponding to the effect of anharmonicity. The bulk modulus K_0 at normal volume appears in eq. 14 by virtue of the expression

$$v_0 = (3^{1/2}c^{1/3}/2^{1/2}\pi)m^{-1/2}v_0^{1/6}K_0^{1/2} \quad (16)$$

where v_0 is the normal volume per atom or molecule. The relation 16 of Gilvarry¹⁸ is essentially equivalent to the characteristic frequencies

evaluated by Madelung¹⁹ and Einstein²⁰ in terms of elastic parameters.

(19) E. Madelung, Physik. Z., 11, 898 (1910).

(20) A. Einstein, Ann. Physik, 34, 170, 550 (1911).

One observes that the final result for the pressure is independent of the constant c of eq. 12 and 13, which depends on details of the structure of the particular solid or liquid. If B is set equal to zero in Hudleston's equation, use of eq. 3 for A yields eq. 14 directly, when one notes that L is proportional to $V^{1/3}$.

Replacing the multiplicative correction factor 15 by the exponential which coincides with it through linear terms, one derives

$$P = 3K_0 \left[\left(\frac{V_0}{V} \right)^{2/3} - \left(\frac{V_0}{V} \right)^{1/3} \right] \exp \left\{ 3\gamma_0 \left[1 - \left(\frac{V}{V_0} \right)^{1/3} \right] \right\} \quad (17)$$

as the formulation of Hudleston's equation in terms of P and V , rather than P and L . For any temperature negligibly removed from absolute zero, eq. 17 is valid when P and V are understood as thermal averages. The derivation is rigorous on the basis of eq. 6 for the energy of an oscillator, apart from the mathematical artifice of replacing a linear form by an exponential. As a consequence of this approximation, the constant γ_0 appearing in the exponential can be strictly identified as a Grüneisen parameter only if the form 17 is fitted to data corresponding to the neighborhood of the energy minimum for the solid. If it is fitted to data spanning a large range of pressure, γ_0 becomes an average

Grüneisen parameter.²¹ In a form analogous to that of eq. 2, one obtains

(21) J. J. Gilvarry, Phys. Rev., 102 325 (1956).

$$\ln \left\{ P \left[\left(\frac{V_0}{V} \right)^{2/3} - \left(\frac{V_0}{V} \right)^{1/3} \right]^{-1} \right\} = \ln(3K_0) + 3\gamma_0 \left[1 - \left(\frac{V}{V_0} \right)^{1/3} \right] \quad (18)$$

Thus, the constants K_0 and γ_0 of the Hudleston equation in the form 17 can be evaluated graphically as simply as for the case of eq. 2.

It has been shown by Druyvesteyn and Meyering²² and by Gilvarry¹⁸

(22) M. J. Druyvesteyn and J. L. Meyering, Physica, 8, 851 (1944).

that the Grüneisen parameter γ for a solid (or liquid) of independent pairs of bond oscillators is given in the general case by

$$\gamma = -\frac{1}{2} \left[\left(\frac{\partial \ln K}{\partial \ln V} \right)_T + 1 \right] \quad (19)$$

where K is the bulk modulus and T is the absolute temperature.

Application of this result to the general formulation 17 of Hudleston's equation yields

$$\lim_{P \rightarrow 0} \gamma = \gamma_0 \quad (20)$$

in the limit of zero pressure, consistently with the conclusion that the constant γ_0 can be identified with the Grüneisen constant only for compressions in the neighborhood of the energy minimum for the body. Thus, the results agree with the identification of the correction factor 15 as representing the effect of anharmonicity on the pressure in the

neighborhood of this minimum. Note that the limit 20 arises entirely from the presence of the exponential factor in eq. 17.

Comparison of eq. 2 and 17 yields

$$B = 3(\log_{10} e)\gamma_0/L_0 \quad (21)$$

for the Hudleston parameter B in terms of the Grüneisen parameter γ_0 of the solid or liquid. By eliminating L_0 between eq. 3 and 21, one obtains the expression

$$\gamma_0 = 10^A B/9(\log_{10} e)K_0 \quad (22)$$

for the Grüneisen constant in terms of the Hudleston parameters and the bulk modulus. Because of the difficulty already noted in the dimensionality of A and B , eq. 22 is essentially a numerical relation, and one cannot verify directly that it is consistent with the dimensionless character of γ_0 . However, if L and L_0 in eq. 2 are assumed dimensionless (as is frequently done), then B can be viewed as dimensionless likewise, and use of eq. 3 yields the simple relation

$$\gamma_0 = (3 \log_{10} e)^{-1} B \quad (23)$$

which is dimensionally correct.

It has been emphasized that Hudleston's equation corresponds physically to a body composed of independent bond oscillators. As such, an artificial element enters the model, since it corresponds essentially to an Einstein solid. It is a matter of some interest to determine the form of the corresponding equation when coupling of the atomic or molecular oscillations is included. Coupling can be taken into account in a simple manner by means of the Debye model, in which the effect of the

actual atomic or molecular vibrations is represented by acoustic oscillators corresponding to elastic waves propagating in the body (viewed as a continuum).^{7,13} In terms of elastic parameters, the Grüneisen parameter on the Debye theory is given by the Slater relation⁶

$$\gamma = -\frac{1}{2} \left(\partial \ln K / \partial \ln V \right)_T - \frac{1}{6} \quad (24)$$

which differs from eq. 19 for a model of independent bond oscillators. Equating this expression to zero, one obtains

$$P = 3K_0[(V_0/V)^{1/3} - 1] \quad (25)$$

as the corresponding equation of state of an ideal harmonic body, containing no anharmonic contribution to the pressure; the corresponding Grüneisen constant is identically zero at any pressure on the basis of the derivation. One verifies easily that inclusion of the multiplicative correction factor 15, with γ_0 a constant, yields the result of eq. 20 at zero pressure when eq. 24 is applied. The artifice of replacing the correction factor by the exponential which agrees with it through linear terms gives

$$P = 3K_0 \left[\left(\frac{V_0}{V} \right)^{1/3} - 1 \right] \exp \left\{ 3\gamma_0 \left[1 - \left(\frac{V}{V_0} \right)^{1/3} \right] \right\} \quad (26)$$

as the analog of Hudleston's equation for the case where the effect of coupling of the oscillations of the atoms or molecules is included in the model. Thus, the generalization 26 of Hudleston's equation stands in relation to the original equation as a many-body theory does to an independent-particle model.

For the same value of K_0 , one finds that the effect of coupling is to reduce the pressure below that corresponding to the case of independent bond oscillators.²³ Whether eq. 26 yields an improved fit of

(23) The two expressions agree through terms of order $(V_0 - V)/V_0$ in view of the definition of the bulk modulus, and hence the difference appears in terms of order $[(V_0 - V)/V_0]^2$.

experimental data over that provided by Hudleston's equation is a moot question. However, eq. 26 without the exponential factor coincides in form with that obtained by Murnaghan from the linear theory of finite strain.²⁴ He found that the expression yielded excellent agreement with

(24) F. D. Murnaghan, "Finite Deformation of an Elastic Solid," John Wiley and Sons, Inc., New York, N. Y., 1951, Chapter 4.

experimental data for both solids and liquids. Note that the constants K_0 and γ_0 in eq. 26 can be evaluated graphically by writing it in a form analogous to eq. 18.

One can observe that the pressure as given by eq. 14 and 25, without the correction factor 15, yields a vanishing contribution to the Grüneisen parameter at zero pressure, consistently with the fact that these forms correspond to the harmonic contribution to the pressure. Hence, in view of Grüneisen's law

$$\gamma = \alpha K V / C_V \quad (27)$$

for γ in terms of the thermal expansion coefficient α (where C_V is the heat capacity at constant volume) the results are consistent with

the fact that an ideal harmonic body (composed of purely harmonic oscillators) exhibits no thermal expansion. This statement can be verified either from the virial theorem for an assemblage of harmonic oscillators, or by direct computation of the thermal average of $r - r_0$ from u of eq. 6 on the basis of classical statistics (which yields Grüneisen's law with $C_V = 3k$, where k is Boltzmann's constant).¹⁸

CASE OF FINITE TEMPERATURE

It is clear that the preceding discussion does not yield an explicit expression for the Helmholtz free energy of the solid or liquid. This lack could be remedied by using the general results of the Grüneisen theory of solids to include a thermal contribution to thermodynamic functions.^{5,6} Instead, the effect of variable temperature in Hudleston's equation of state will be included by a phenomenological method described in the general case by Gilvarry,^{16,17} to yield a result closely similar to that already appearing in the literature for Hudleston's equation.

Define a dimensionless parameter η by

$$\eta = K\alpha^{-1}(\partial\alpha/\partial P)_T \quad (28)$$

where α is the volumetric coefficient of thermal expansion. In view of the thermodynamic identity²⁵

$$(25) \text{ F. Birch, } \underline{\text{J. Geophys. Res.}}, \underline{57}, 227 \text{ (1952).}$$

$$\eta\alpha = -K^{-1}(\partial K/\partial T)_P \quad (29)$$

it is clear that $\eta\alpha$ is the temperature coefficient of the bulk modulus at constant pressure. Let η_0 and α_0 denote values of η and α ,

respectively, corresponding to zero pressure but depending on temperature, and let $K_{0,t}$ and $V_{0,t}$ represent values of K and V , respectively, evaluated at zero pressure and an arbitrary reference value t of the absolute temperature T . Then, the dominant contribution of eq. 14 to the pressure in the Hudleston equation of state becomes

$$P = 3K_{0,t} \exp\left[-\int_t^T \eta_0 \alpha_0 dT\right] \cdot \left[\left(\frac{V_{0,t}}{V} \exp \int_t^T \alpha_0 dT\right)^{2/3} - \left(\frac{V_{0,t}}{V} \exp \int_t^T \alpha_0 dT\right)^{1/3}\right] \quad (30)$$

for arbitrary temperature T . The argument of the exponential in the correction factor appearing in eq. 17 becomes

$$3\gamma_0 \left\{ 1 - \left[\frac{V}{V_{0,t}} \exp\left(-\int_t^T \alpha_0 dT\right) \right]^{1/3} \right\} \quad (31)$$

directly from Gilvarry's results.

The form of Hudleston's equation for variable temperature used by Bett,² by Bett, Hayes, and Newitt,³ and by Bett, Weale, and Newitt⁴ corresponds essentially to eq. 30 when multiplied by an exponential with the argument 31, but with the salient omission of the exponential factor depending on the integral of $\eta_0 \alpha_0$ with respect to temperature. As shown by Gilvarry,¹⁶ this correction factor is essential for a correct result. These prior discussions neglected the fact that the bulk modulus as well as the volume must be corrected for a change in temperature. However, it can be noted that the correction factor on the volume depending on the integral of α_0 with respect to temperature is dominant in eq. 30 at low pressure over the correction to the bulk modulus represented

by the exponential depending on the integral of $\eta_0 \alpha_0$ with respect to temperature. As a consequence, only an approximate value of η_0 may be sufficient for adequate accuracy in the representation of the data for P .

In the integrals appearing in these expressions, the integrands α_0 and $\eta_0 \alpha_0$ must correspond to zero pressure; in this case, eq. 30 as it stands is thermodynamically correct through terms of order P/K_0 as parameter of smallness.¹⁶ If the paths of integration cross the fusion point, the integrands at this point must be understood as proportional to delta functions, with the coefficients chosen to yield the proper change in volume and discontinuity in bulk modulus for melting at the temperature of fusion in question. Thus, t may correspond to absolute zero, and T may represent a temperature corresponding to the liquid phase. For a solid with a normal fusion curve, the method of determining values α_0 and $\eta_0 \alpha_0$ of α and $\eta \alpha$, respectively, to correspond to zero pressure for temperatures above the fusion value for a particular pressure has been discussed by Gilvarry.¹⁶ It is clear that the exponentials appearing can be replaced by linear forms when the range of integration from t to T is sufficiently small and does not include the fusion point. In this case, the volume $V_{0,T}$ and bulk modulus $K_{0,T}$ at zero pressure but arbitrary temperature can be written as

$$V_{0,T} = V_{0,t} [1 + \alpha_0 (T - t)] \quad (32)$$

$$K_{0,T} = K_{0,t} [1 - \eta_0 \alpha_0 (T - t)] \quad (33)$$

respectively. If experimental data for different isotherms are plotted to correspond to the two sides of the equation

$$\ln \left\{ P \left[\left(\frac{V_{O,T}}{V} \right)^{2/3} - \left(\frac{V_{O,T}}{V} \right)^{1/3} \right]^{-1} \right\} = \ln(3K_{O,T}) + 3\gamma_c \left[1 - \left(\frac{V}{V_{O,T}} \right)^{1/3} \right] \quad (34)$$

values of $K_{O,T}$ as determined graphically yield values of η_0 directly from eq. 33. Tables of values of η_0 are available for solids,^{5,25,26}

(26) J. J. Gilvarry, Phys. Rev., 102, 308 (1956).

but the author is unaware of similar compilations for liquids.

One may note that the derivation of the argument 31 of the exponential makes use of the usual assumption that the Grüneisen parameter is independent of temperature.¹⁷ To check consistency, one can apply eq. 19 to the generalized form of Hudleston's equation, including the effect of temperature. One obtains

$$\lim_{P \rightarrow 0} \gamma(T) = \gamma_0 \quad (35)$$

as the constant limiting value of $\gamma(T)$ at zero pressure, independently of the absolute temperature T . In general, therefore, the exponential correction factor with argument 31 as applied to eq. 30, or the exponential factor in Hudleston's eq. 1, represents the effect of anharmonicity on the pressure in the neighborhood of the minimum in the Helmholtz free energy at arbitrary fixed temperature.²⁷ Further, comparison of eq. 23

(27) The results are not entirely self-consistent, since $\gamma(T)$ from either eq. 30 or the following eq. 37 shows a slight temperature sensitivity depending on $\alpha_0(T - t)$, which is cancelled at zero pressure by a term depending on V , as $V = V_0[1 + \alpha_0(T - t)]$ in this limit. This difficulty in the case of Birch's equation has been discussed elsewhere by Gilvarry.¹⁷

with eq. 35 yields

$$\lim_{P \rightarrow 0} \gamma(T) = (3 \log_{10} e)^{-1} B \quad (36)$$

for any isotherm. It follows from the constancy of γ_0 in eq. 23 that the Hudleston parameter B should be independent of temperature. This conclusion is in accord with the experimental data of Hudleston,¹ of Bett,² of Bett, Hayes, and Newitt,³ and of Bett, Weale, and Newitt.⁴

The foregoing argument presupposes that the Grüneisen parameter is independent of temperature, on Grüneisen's postulate that the lattice frequencies of a solid are a function only of the volume.^{5,6} The experimental evidence on this point is conflicting for low temperatures (approaching absolute zero),¹⁶ but the bulk of the data for solids at normal temperature and higher do seem to indicate that γ is independent of temperature,^{25,26} at least approximately. On a similar assumption that the characteristic frequencies of a liquid are a function mainly of the volume (near the solidification curve in any event), one concludes that γ is an approximate constant with respect to temperature. In the case of either a solid or liquid, therefore, one obtains the experimentally verified conclusion that the parameter B in Hudleston's equation of state is a constant independently of the particular isotherm considered.

The form 26 of Hudleston's equation as generalized to include coupling can be extended easily to include the effect of variable temperature. For the dominant contribution to the pressure, one obtains

$$P = 3K_{0,t} \exp \left[- \int_t^T \eta_0 \alpha_0 dT \right] \cdot \left[\left(\frac{V_{0,t}}{V} \exp \int_t^T \alpha_0 dT \right)^{1/3} - 1 \right] \quad (37)$$

as generalized to an arbitrary temperature T . The argument of the exponential correction factor remains as given by 31 for Hudleston's equation. In this form, the generalized equation of state yields the result of eq. 35 for γ at zero pressure and arbitrary temperature, when eq. 24 for the Grüneisen parameter on the Debye model is applied. Thus, comparison with experimental data should yield a value of the parameter γ_0 independent of the particular isotherm, at least if the fit is restricted to the range of small pressure in the neighborhood of the minimum in Helmholtz free energy for the body.

It has been noted that the pressure as given by eq. 14 and 25 in the case of zero temperature, without the correction factor 15, yields a vanishing contribution to the Grüneisen parameter in the limit $P \rightarrow 0$, since it represents the harmonic part of the pressure. One can show that a similar result holds for eq. 30 or eq. 37 with neglect of the correction factor depending on the argument 31, for the case of finite temperature in the limit of zero pressure. Thus, the limit 35 arises entirely from the presence of the exponential factor. Hence, in view of Grüneisen's law of eq. 27, the thermal expansion coefficient α_0 in eq. 30 and 37 vanishes if γ_0 vanishes, and the results are approximately consistent at finite temperature with the requirement that an ideal harmonic body display no thermal expansion.²⁷

COMPARISON WITH EXPERIMENT

A check on the basic validity of the derivation of Hudleston's equation presented can be obtained by comparing values of the Grüneisen constant from eq. 22 with values obtained by other means. For this

purpose a liquid obviously provides a more stringent test than a solid, since application of the Grüneisen theory to a liquid involves an extension of its domain of validity as usually understood. Bett² has determined the values of the Hudleston parameters for liquid mercury by analysis of compression data of Bridgman over a pressure range of 1 to 10 kilobars, for temperatures of 0°C. and 22°C., and obtains $B = 4.95$. The corresponding value of γ_0 can be obtained from eq. 23, since Bett treats L and L_0 as dimensionless; it appears as the first entry in the last column of Table I. The second entry in this column was obtained by application of Grüneisen's law of eq. 27 to the solid at fusion.²⁶ The final entry corresponds to Gilvarry's relation²⁶

$$\gamma_m = \frac{1}{2} q K_m \frac{\Delta V}{L} \quad (38)$$

for the Grüneisen constant γ_m of a solid at fusion, where K_m is the bulk modulus of the solid at melting, ΔV and L are the volume change and latent heat of fusion, respectively, and q is a constant which does not differ greatly from unity. The value of γ_m in eq. 38 has been corrected by the subtractive constant $1/3$ from that given originally,²⁶ to correspond to eq. 19 for a model of independent bond oscillators, rather than to eq. 24 for the Debye theory.¹⁸

The last two entries in the final column of Table I correspond to solid mercury at melting and hence to a temperature of -38.9°C., whereas the value obtained from eq. 23 refers to a temperature range from 0 to 22°C. However, the results show that extension of the Grüneisen theory to liquids yields a value of the Grüneisen constant for liquid mercury reasonably concordant with values for the solid at fusion.

Bett, Weale, and Newitt⁴ have given a compilation of thermodynamic parameters for liquid mercury, sufficient to determine the temperature variation of γ from Grüneisen's law. Values of the relevant parameters for three temperatures are given in Table II; the results for C_V were obtained from C_P by means of the thermodynamic identity

$$C_V = C_P - \alpha^2 KVT \quad (39)$$

The values of γ appearing in the last column agree with values from Table I within limits which are reasonable for a comparison of Grüneisen parameters of solids, as obtained from different theoretical determinations.^{6,26} Moreover, the very slow variation of the Grüneisen parameter with temperature apparent from Table II is consonant with the observed insensitivity to temperature of the Huddleston parameter B .

Grüneisen constants for solids can be determined from the parameters a and b in the Bridgman equation of state

$$(V_0 - V)/V_0 = aP - bP^2 + \dots \quad (40)$$

On the basis of eq. 19, one has

$$\gamma_0 = b/a^2 - 1 \quad (41)$$

Experimentally, the coefficient b is difficult to determine accurately. Bett, Hayes, and Newitt³ have summarized the available data on the Bridgman parameters of liquid mercury. From the results of six investigations, they find a mean value for b which appears in the first line of Table III, with the standard deviation shown. Relatively, the error in a is insignificant. The corresponding value of γ_0 with its standard deviation is shown in the last column of the table, and one sees

that γ_0 of Table I equals this value within the limits of error. The extreme low and extreme high values of γ_0 in the compilation of Bett, Hayes, and Newitt (lying outside the range specified by the standard deviation) were ignored, and the mean and the standard deviation of the remaining three were computed, to yield the result shown in the second line. One sees that the corresponding value of γ_0 in the last column agrees reasonably, within the limits for the standard deviation shown, with the result of Table I.

The numerical agreement obtained is by no means perfect. On the other hand, it is essential to realize that exact agreement between γ from Grüneisen's law and from eq. 19 is not demanded by theory, because of the effect of the simplifying assumptions which enter the argument.⁶ Equations 23 and 41 actually yield average Grüneisen parameters, since the corresponding equations of state are fitted to data covering a finite range of pressure. As such, the corresponding values of γ_0 tend to exceed values inferred from data in the neighborhood of the energy minimum or from Grüneisen's law, consonantly with a behavior noted elsewhere.²¹

CORRESPONDENCE OF LIQUID AND SOLID STATES

In this section, an explicit demonstration of the close correspondence between equations of state for the solid and liquid near the melting point will be given.

From the results of Bett, of Bett, Hayes, and Newitt, and of Bett, Weale, and Newitt, it is clear that liquid mercury obeys Hudleston's equation over the temperature range 0 - 22°C., which is not far removed from the absolute temperature of solidification. Although experimental

data are lacking for other metals, it is reasonable to assume that the data for the pressure vs. volume of any one monatomic liquid metal will satisfy the equation near the solidification temperature. In particular, one expects this conclusion to hold for the liquid alkali metals, since the melting points in the family range from 29.7° to 136°C . from Cs to Li, respectively, and thus fall reasonably in the range where Hudleston's equation has been found applicable. Thus, an idea of the general degree of correspondence between the equations of state of the liquid and the solid near the melting point can be obtained by comparing Hudleston's equation (presumed valid for the liquid alkali metals) with the theoretical and experimental results for the pressure vs. volume in the solid alkali metals.

The equations of state for the alkali metals in the solid phase have been calculated by Bardeen from quantum mechanics by the Wigner-Seitz method under certain approximations.²⁸ His result for the dominant

(28) J. Bardeen, J. Chem. Phys., 6, 372 (1938).

contribution to the pressure is

$$P = 3K_0[(V_0/V)^{5/3} - (V_0/V)^{4/3}] \quad (42)$$

requiring a multiplicative correction at the higher compressions given by

$$1 + \zeta[(V_0/V)^{1/3} - 1] \quad (43)$$

with ζ a constant. Bardeen compared his results with experimental data of Bridgman for Cs, Rb, K, Na, and Li extending to pressures of 45 kilobars and corresponding to room temperature. Excellent agreement was found, in general, and the effect of the correction ⁴³ was found to be small.

In the case of at least one alkali metal (Cs, which melts at 29.7°C.), the conclusions are valid near the fusion point; they hold at temperatures reasonably near that of fusion for Rb and K, and to a less extent for Na and Li.

Factoring out V_0/V in Bardeen's eq. 42, one obtains

$$P = (V_0/V) \{ 3K_0 [(V_0/V)^{2/3} - (V_0/V)^{1/3}] \} \quad (44)$$

where the expression in braces is simply Hudleston's result for the pressure, without the exponential correction factor. Now, K_0 and V_0 represent the bulk modulus and volume at zero pressure, respectively, and the discontinuity in these parameters at the fusion point is small relative to their values. Thus, Bardeen's equation applied to a solid alkali metal near the fusion point differs from Hudleston's equation for a liquid alkali metal near the crystallization point only by the factor V_0/V , in which V_0 can be evaluated indifferently for the solid or liquid as a first approximation. However, V_0/V can be expanded in a Taylor series as

$$V_0/V = 1 + P/K_0 + \dots \quad (45)$$

from the definition of the bulk modulus. For the alkali metals at melting, the values of K_0 for the solid phase range from 2×10^4 to 1×10^5 bar from Cs to Li, respectively.^{26,29} Hence, P/K_0 does not exceed

(29) J. J. Gilvarry, J. Chem. Phys., **23**, 1925 (1955).

about 10% for any alkali metal, for P up to 1 kilobar. Accordingly, on the assumption that Hudleston's equation is valid for the liquid alkali metals near the solidification point, it differs from the quantum mechanical result for the solids near fusion, in analytic form and value,

only by a factor differing from unity by 10% at most up to a pressure of 1 kilobar (when the correction factors are neglected in each case). This quantitative result justifies the basic assumption of this paper, that the statistical and quantum mechanics of the solid represent a proper point of departure in inferring the equation of state for a liquid near the crystallization point.

A similar argument can be used to show consistency of Hudleston's equation for a liquid with Birch's equation of state for a solid, derived from the theory of finite strain.^{25,30} Birch has shown that his

(30) F. Birch, Phys. Rev., 71, 809 (1947).

expression yields better agreement with experimental data for the alkali metals at the very highest pressures available (about 0.1 megabar) than does Bardeen's result.

DISCUSSION AND CONCLUSIONS

It can be noted that all the equations of state considered show a certain similarity. Thus, Hudleston's equation, this result as generalized here to apply to coupled vibrations, and the Bardeen and Birch equations all have a dominant binomial in $(V_0/V)^{1/3}$ as common elements in their analytic form. All the equations require modification of the dominant binomial by a correction factor which becomes relatively important only for the higher compressions. It is worthy of note that the dominant binomial in each case can be reduced for pressures approaching zero to the form of eq. 25. This equation of state corresponds to an ideal harmonic body on the Debye theory, or to the result of Murnaghan's linear theory of finite strain.

Of the equations of state considered, however, only Bardeen's shows the proper analytic form in the limit of very high compression (at a pressure exceeding some limit in the neighborhood of megabars). This result can be shown by a simple argument from the virial theorem³¹

(31) J. C. Slater, J. Chem. Phys., 1, 68 (1933).

$$\frac{3}{2} PV = E_{\text{kin}} + \frac{1}{2} E_{\text{pot}} \quad (46)$$

of quantum mechanics, where E_{kin} and E_{pot} are the total kinetic and potential energies of the electrons of an atom, respectively (the thermal motion of the nucleus is ignored). Consider the limit of very high pressure where the electron distribution corresponds to a degenerate Fermi-Dirac gas. In this limit of small volume, the kinetic and potential energies of an electron vary as $1/r^2$ and $1/r$, respectively, in terms of some radius r of the atom.³² Inserting this functional dependence into

(32) J. J. Gilvarry, Phys. Rev., 96, 934 (1954).

eq. 46, one obtains

$$P = aV^{-5/3} - bV^{-4/3} \quad (47)$$

where a and b are positive constants. This result has precisely the analytic form of the dominant contribution of eq. 42 to the pressure in Bardeen's equation.

Evaluating the constants a and b in eq. 47 by requiring that the pressure vanish and the bulk modulus have the normal value K_0 when the volume equals V_0 , one obtains a heuristic derivation of Bardeen's equation. In a similar manner one can derive the equation from the old quantum theory of Bohr for the hydrogen atom (which is alkali-like), by

evaluating E_{kin} and E_{pot} of eq. 46 on this model. However, such derivations are no more than heuristic since the constants a and b in eq. 47 are fixed at very high compression by the Thomas-Fermi statistical model of the atom in terms of atomic constants^{32,33} (rather than K_0 and V_0).

(33) N. H. March, Proc. Phys. Soc., A68, 726 (1955).

These considerations delimit the range of validity of Hudleston's equation and the variant involving the effect of vibrational coupling given here, as well as the temperature-dependent forms obtained. At some pressure exceeding a limit in the order of megabars, these results must lose validity, since the dominant exponential behavior of Hudleston's expression at high pressure does not coincide with the result of eq. 47 demanded by quantum statistical mechanics, as inferred from the Thomas-Fermi statistical atom model. Hence, the replacement of a linear form involving the Grüneisen constant by an exponential coinciding with it through linear terms, which is the crux mathematically of the derivation of Hudleston's equation given here, can be valid only through an intermediate range of pressure. Teller³⁴ has hypothesized that the pressure

(34) E. Teller, Trans. American Geophys. Union, National Research Council - National Academy of Sciences, 1937, p. 54.

in this intermediate region should vary exponentially with the change in volume; his argument is based on the exponential decrease of the electron density in the outermost part of an atom or molecule. A similar conclusion was reached by Levitt³⁵ on purely empirical grounds. For low pressure,

(35) L. S. Levitt, J. Phys. Chem., 58, 573 (1954).

eq. 1/ becomes exact for a model of independent bond oscillators, and the corresponding result 26 is correct if the oscillations are coupled. On a priori grounds, one should expect the form taking the effect of coupling into account to yield a better agreement with observed data, but this is a matter for experimental decision. However, it can be noted that the form 24 of the Grüneisen parameter corresponding to the Debye model yields better agreement with values inferred from Grüneisen's law than does the result 19 for independent oscillators, for an average taken over 19 elements in the solid state.¹⁸

It is clear from the present results that Hudleston's equation for a liquid follows directly from the formal extension to this case of the Grüneisen theory of characteristic vibrations of a solid. The theory yields an immediate explanation of the lack of temperature dependence observed for the Hudleston parameter B , and correlates its value with other physical parameters of the liquid. In principle, the model coincides with that adopted by Mott in treating the electrical conductivity, and by Andrade in discussing the viscosity of liquids. As such, the basic idea is that a liquid near crystallization is far more similar to a solid than it is to a gas. The merit of simple models like the one treated here lies in yielding explicit if only approximately quantitative results in areas where application of the general methods of Born and Green and of Kirkwood is far too difficult.

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Table I: Values of Grüneisen Constants for Liquid and Solid Mercury

Parameter	Phase	Temp. °C.	Grüneisen constant
γ_0 , eq. 23	Liquid	0-22	3.80 ^a
γ , eq. 27	Solid	-38.9	2.1 ^b
γ_m , eq. 38	Solid	-38.9	2.9 ^b

^aValue corresponding to $B = 4.95$ of Bett (ref. 2). ^bValue of Gilvarry (ref. 26).

Table II: Temperature Variation of the Grüneisen Parameter for Liquid Mercury, From Grüneisen's Law

Temp. °C.	$v \times 10^2$ cm ³ /g	$\alpha \times 10^4$ °C. ⁻¹	$K \times 10^5$ bar	C_p joule/g°C.	C_v joule/g°C.	γ
0	7.3556	1.8145	2.550	0.1405	0.1236	2.753
10	7.3692	1.8131	2.520	0.1401	0.1229	2.741
20	7.3882	1.8118	2.491	0.1397	0.1220	2.733

Table III: Values of Grüneisen Constants for Liquid Mercury, From Bridgman Parameters

Mean	$b \times 10^{10}$ bar ⁻² ^a	$a \times 10^6$ bar ⁻¹ ^b	γ_0
Of 6	1.10 ± 0.70	3.91 ± 0.10	6.3 ± 5.0
Of 3	0.83 ± 0.31	3.91 ± 0.10	4.4 ± 2.0

^aTemperature, 25°C. ^bTemperature, 20°C.